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Oxidation of Olefins by Palladium(II). VII. Comparison of Palladium(II) Chloride with Other Noble Metal Salts in the Copper(II) Chloride Promoted Oxidation in Acetic Acid[1]

Patrick M. Henry[2]

The Research Center, Hercules Incorporated, Wilmington, Delaware 19899

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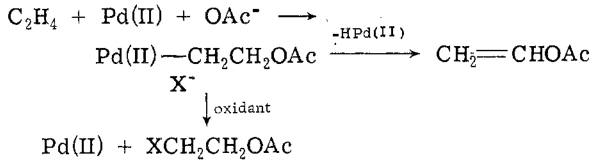
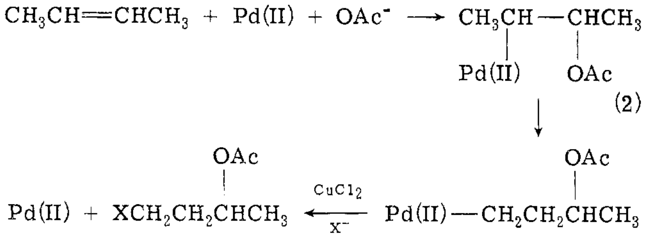
Studies of the $CuCl_2$-promoted oxidation of olefins to chloro- or diacetates by $PdCl_2$ in acetic acid have been extended to other noble metal chlorides. $PtCl_2$ was found to be more effective than $PdCl_2$ in the oxidation of cyclohexene to saturated esters, whereas $RhCl_3$ and $IrCl_3$ were less active than $PdCl_2$. $PtCl_2$ gave almost exclusively 1,2-disubstituted cyclohexanes, while $PdCl_2$ and $RhCl_3$ gave appreciable amounts of 1,3 and 1,4 isomers along with the 1,2 isomers. The ratios of chloro- to diacetates, as well as the distribution of geometric isomers, was also quite different for the four noble metal salts which gave saturated esters. $PtCl_2$ also oxidized 1-butene exclusively to 1,2 isomers and *cis*- and *trans*-2-butene exclusively to 2,3 isomers. The product distributions were again quite different from those obtained with $PdCl_2$ under the same reaction conditions in regard to positional isomerism, geometric isomerism, and ratios of chloro- to diacetates. The results of this study provide evidence against a mechanism involving alkyl transfer from noble metal to Cu(II).

The oxidation of olefins to saturated ester or ether products by Pd(II) salts plus other oxidants, such as $CuCl_2$, $Tl(OAc)_3$, $Pb(OAc)_4$, $AuCl_3$, NO_3^-, KCr_2O_7, Br_2, or Cl_2 has now been the subject of several studies.[1,3-13] The most reasonable mechanism consistent with other palladium chemistry appears to be capture of an oxypalladation intermediate by the oxidant to give the saturated products instead of the unsaturated products found in the absence of oxidant. For ethylene in acetic acid, the reaction scheme would be given by equation 1 (X = OAc or Cl)



$$C_2H_4 + Pd(II) + OAc^- \longrightarrow \underset{X^-}{Pd(II)-CH_2CH_2OAc} \xrightarrow{-HPd(II)} CH_2{=}CHOAc \quad (1)$$
$$\underset{X^-}{Pd(II)-CH_2CH_2OAc} \xrightarrow{\text{oxidant}} Pd(II) + XCH_2CH_2OAc$$

When higher olefins are used, products are formed[5,9] which must have resulted from movement of Pd(II) down the carbon chain before reacting with oxidant. Thus 2-butene gives 1,3- as well as 1,2-disubstituted butenes when oxidized by the $PdCl_2$–$CuCl_2$ system in acetic acid. The

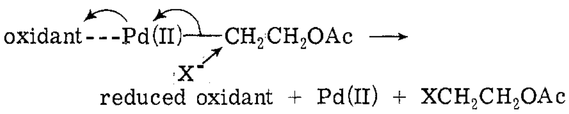


$$CH_3CH{=}CHCH_3 + Pd(II) + OAc^- \longrightarrow CH_3\underset{Pd(II)}{CH}-\underset{OAc}{CHCH_3} \longrightarrow Pd(II)-CH_2CH_2\underset{OAc}{CHCH_3} \xrightarrow[X^-]{CuCl_2} Pd(II) + XCH_2CH_2\underset{OAc}{CHCH_3} \quad (2)$$

movement down the chain almost certainly occurs by Pd(II) hydride eliminations and readditions.

The reason for the change in product distribution in the presence of oxidant is most likely related to the nature of decomposition of Pd(II) alkyls. Since monomeric Pd(0) is an unstable species, the Pd(II)–carbon bond does not break heterolytically to give Pd(0) and a carbonium ion. Rather Pd(II) hydride is eliminated to give olefin. The oxidant is believed to facilitate the heterolytic decomposition of the Pd(II)–carbon bond by avoiding the necessity of forming Pd(0), thus giving substitution rather than elimination products.

The exact means whereby the oxidant accomplishes this change in product distribution is not certain and may differ for different oxidants. Possibilities are (1) transfer of alkyl to oxidant followed by decomposition; (2) oxidation transfer of alkyl to oxidant followed by decomposition; (2) oxidation of Pd(II) to Pd(IV) followed by decomposition; and (3) removal of electrons from the Pd(II) as the Pd(II)–carbon bond is being broken.



$$\text{oxidant}---Pd(II)-\underset{X^-}{CH_2CH_2OAc} \longrightarrow \text{reduced oxidant} + Pd(II) + XCH_2CH_2OAc \quad (3)$$

One possible means of distinguishing between the first and the other two possibilities is the use of other noble metal salts as replacements for Pd(II). If complete transfer of the organic moiety to oxidant occurs, the product distribution for a given positional isomer should be independent of the noble metal used.

The purpose of this study is to determine if other noble metal salts can be used in place of $PdCl_2$ in the $CuCl_2$-promoted reaction and to see if the product distributions vary from one noble metal to another.

Results

The activity of the other noble metal salts in the $CuCl_2$-promoted oxidation of olefins was first tested using cyclohexene as substrate. Reaction times of only 1 hr at 75° were used to ensure products were primary oxidation products. Results are given in Table I. The formation of saturated products is an indication of activity of the noble metal salt. By this criterion $RuCl_3$[14] and $OsCl_3$ are inactive, while $IrCl_3$ and $RhCl_3$ have low activity. $PtCl_2$ was more reactive than $PdCl_2$ in producing saturated ester.

$PtCl_2$ and $RhCl_3$ were chosen for further study. In Table II are given the product distributions for cyclohexene oxidation under two sets of reaction conditions. Longer reaction times were used to increase conversions, thus enabling more accurate product distribution determinations. Once again $PtCl_2$ is most active for production of saturated esters, while $PdCl_2$ is most active for production of unsaturated esters. $PtCl_2$ also gives the simplest product distributions. At low chloride concentrations, only one unsaturated and two of the three possible 1,2 isomers are formed. No 1,3 or 1,4 isomers were detected. $PdCl_2$ and $RhCl_3$ gave 1,2, 1,3, and 1,4 isomers with the product distributions most complicated for $PdCl_2$. At high chloride, the same general trends are observed except that $PtCl_2$ does now give small amounts of other positional isomers as well as *cis*-1,2-chloroacetate. The product distributions with $PdCl_2$ and $RhCl_3$ also display more positional isomerization. With both, the

Table I
Test of Various Noble Metals for Oxidation of Cyclohexene with Cupric Chloride at 75°[a]

Products	Concentration, 10^3 M[b]					
	$PdCl_2$	$PtCl_2$	$RhCl_3$	$RuCl_3$	$IrCl_3$	$OsCl_3$
	Unsaturated Esters					
2-Cyclohexen-1-yl acetate	6.0	6.3	4.7	0.73	0.61	4.0
3-Cyclohexen-1-yl acetate	0.5	ND	1.6	ND	ND	1.4
	1,2 Isomers					
trans-Chloroacetate	1.3	4.8	0.12	ND	0.18	ND
cis-Chloroacetate	0.9	ND	ND	ND	ND	ND
cis-Diacetate	0.9	11.8	0.25	ND	0.25	ND
	Other Isomers					
trans-1,3- and -1,4-chloroacetate	0.8	ND	ND	ND	ND	ND
cis-1,4-Chloroacetate	0.06	ND	ND	ND	ND	ND
cis-1,3- and -1,4-diacetate	0.16	ND	ND	ND	ND	ND
trans-1,3-Diacetate	ND	ND	0.1	ND	ND	ND

[a] All contain 0.5 mol of cyclohexene, 1.0 mol of cupric chloride, 0.01 mol of metal salt, and 1.0 mol of lithium acetate per liter of acetic acid and were run for 2 hr. Soluble [Cu(II)] = 0.75 M in this system. [b] 1-Cyclohexen-1-yl acetate and *trans*-1,2- or -1,4-diacetate were not detected in any of the runs; *trans*-1,3- and -1,4-chloroacetates as well as *cis*-1,3- and -1,4-diacetate were not separated by gas–liquid chromatography (glc). ND means not detected. Level of detection is 0.1×10^{-3} M.

Table II
Product Distributions for the Oxidation of Cyclohexene with Three Noble Metal Salts at 75°

Products	Concentration, 10^3 M[c]					
	Low chloride (23 hr)[a]			High chloride (49 hr)[b]		
	$PdCl_2$	$PtCl_2$	$RhCl_3$	$PdCl_2$	$PtCl_2$	$RhCl_3$
	Unsaturated Esters					
2-Cyclohexen-1-yl acetate	86	21	12	5.2	5.4	3.7
3-Cyclohexen-1-yl acetate	71	ND	17	18	0.8	24
	1,2 Isomers					
trans-Chloroacetate	4.4	43	0.5	7.5	35	1.3
cis-Chloroacetate	3.2	ND	ND	11	5.9	0.5
cis-Diacetate	5.3	32	2.2	7.7	63	4.0
	Other Isomers					
trans-1,3- and -1,4-chloroacetate	11	ND	ND	9.8	ND	0.7
cis-1,4-Chloroacetate	0.6	ND	ND	0.8	ND	1.9
cis-1,3- and -1,4-diacetate	7.8	ND	0.4	1.5	14	1.7
trans-1,3-Diacetate	1.2	ND	1.1	0.9	3.1	ND

[a] Reaction mixture identical with that in Table I. [b] Same as low chloride except it also contains 2.0 mol of lithium chloride per liter of acetic acid. This reaction mixture is homogeneous. [c] Same comment as *b* of Table I.

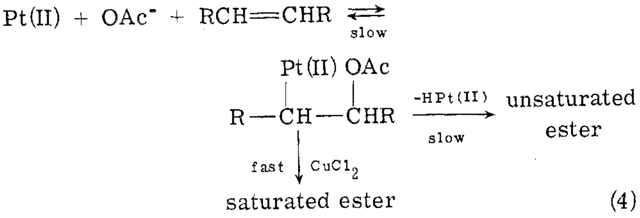
3-cyclohexen-1-yl acetate becomes the main unsaturated product.

Next the oxidation of the butenes by $PdCl_2$ and $PtCl_2$ was studied. Product distributions for $PdCl_2$ under one set of reaction conditions have been reported.[7] Product distributions for oxidation of *cis-* and *trans-* 2-butene under several reaction conditions are given in Table III. The data are presented in terms of ratios of positional and geometric isomers as well as ratios of chloro- to diacetate. These data indicate $PdCl_2$ gives considerable positional isomerization. The ratios of other products do not appear to follow any simple pattern.

The product distributions obtained by oxidation of the butenes by $PtCl_2$ plus $CuCl_2$ for one set of reaction conditions is given in Table IV. No positional isomerization has occurred but *cis-* and *trans-* 2-butene gives mixtures of all possible 2,3 products. Particularly interesting is the fact that the *threo-* chloroacetate is the main product with both olefin isomers.

Discussion

Probably the most unexpected result of this work is the high reactivity of $PtCl_2$ in the $CuCl_2$-promoted reaction since, in general, Pt(II) is less labile than Pd(II). This higher reactivity can probably best be rationalized in terms of a higher steady state concentration of the acetoxymetalation adduct from Pt(II) as compared with the corresponding intermediate from Pd(II). Thus deacetoxymetalation as well as decomposition by Pt(II) hydride elimination would be much slower for Pt(II) than for Pd(II) and the intermediate thus has more opportunity for reaction with $CuCl_2$.



$$\mathrm{Pt(II)} + \mathrm{OAc^-} + \mathrm{RCH{=}CHR} \underset{\text{slow}}{\rightleftarrows} \begin{array}{c} \mathrm{Pt(II)\ \ OAc} \\ \mathrm{|\qquad |} \\ \mathrm{R{-}CH{-}CHR} \\ \text{fast}\ \big\downarrow\ \mathrm{CuCl_2} \\ \text{saturated ester} \end{array} \xrightarrow[\text{slow}]{\mathrm{-HPt(II)}} \begin{array}{c}\text{unsaturated} \\ \text{ester}\end{array} \qquad (4)$$

The lower yields of unsaturated esters and positional isomers with Pt(II) as compared with the other noble metal salts are understandable in terms of the stability of Pt(II) alkyls to decomposition by Pt(II) hydride elimination. As shown in eq 5, both of these products require Pt(II) hydride elimination (X = Cl or OAc).

trans- $Pt(C_2H_5)Cl(PEt_3)_3$ decomposes to *trans-* $PtHCl(PEt_3)_2$ and ethylene only at 180°[15] while Pd(II) alkyls with β hydrogen decompose rapidly at room temperature.[16] The position isomerization of the saturated esters requires readdition of Pt(II) hydride which also does not occur very readily.[15]

The product distributions with the various noble metal salts also provide evidence against one of the possible mechanisms suggested in the introductory paragraph. If

Table III
Effect of Reaction Conditions on Product Distributions for Oxidation of *cis*- and *trans*-2-Butene by $PdCl_2$ Plus $CuCl_2$

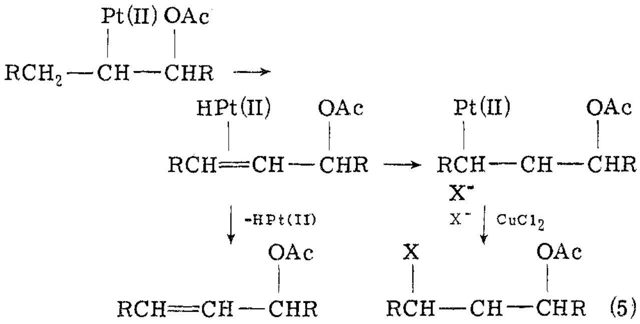
Reaction[a] mixture	Temp, °C	[1,3 isomer]/[2,3 isomer]		[Diacetate]/[chloroacetate] 2,3 isomer		[Diacetate]/[chloroacetate] 1,3 isomer		Chloroacetate [erythro]/[threo]		Diacetate [meso]/[*dl*]	
		Cis	Trans	Cis	Trans	Cis	Trans	Cis	Trans	Cis	Trans
Very low Cl	25	1.6	0.95	4.3	0.81	19	1.4	2.2	4.7	11	0.09
Low Cl	25	0.8	0.22	0.59	0.65	0.63	0.60	0.2	3.5	>10	0.15
High Cl	25	0.11	0.05	0.34	0.44	*b*	1.4	12	0.71	>10	0.15
Very low Cl	100	3.2	2.1	0.21	0.94	0.11	2.7	0.8	2.4	0.65	0.40
Low Cl	100	2.2	0.65	0.51	0.39	0.20	0.22	0.43	2.2	3.6	0.52
High Cl	100	0.17	1.0	0.61	0.33	0.32	0.93	0.75	0.86	8.3	0.22

[a] Low Cl and high Cl corresponds to reaction mixtures of Table II. Very low Cl is same as low Cl except sodium acetate is used in place of lithium acetate. At 25°, atmospheric olefin was used, while at 100°, the pressure was the maximum at this temperature. At 25°, the reaction time was 8 hr, while at 100°, it was 1 hr. [b] No 1,3 isomer was detected.

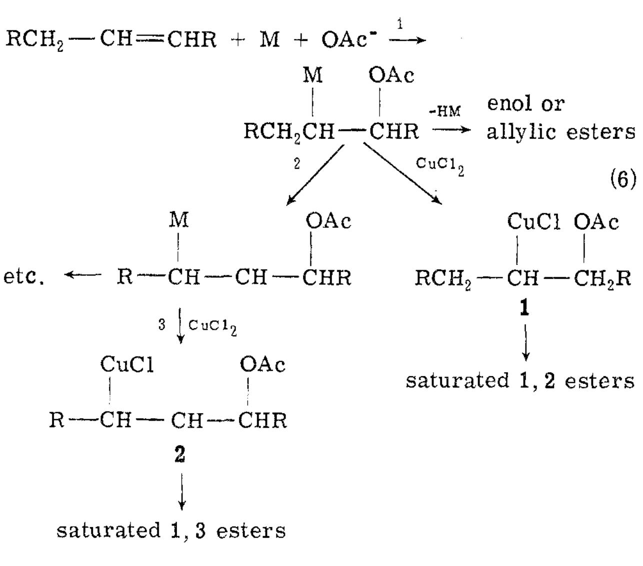
Table IV
Product Distributions from the Oxidation of the Butenes by $PtCl_2$ Plus $CuCl_2$ at 100°[a]

Products	Concentration, 10^3 M[b] *cis*-2-Butene	*trans*-2-Butene	1-Butene
2,3 Isomers			
erythro-Chloroacetate	0.5	1.6	ND
threo-Chloroacetate	15.0	7.8	ND
meso-Diacetate	1.2	1.1	ND
dl-Diacetate	1.1	0.82	ND
1,2 Isomers			
1-Chloro-2-acetoxybutane	ND	ND	20.3
2-Chloro-1-acetoxybutane	ND	ND	4.5
1,2 Diacetate	ND	ND	1.7

[a] Reaction mixture identical with low chloride in Table III. Run for 1 hr at maximum olefin pressure. [b] ND means not detected (<0.1 × 10^{-3} M).



the mechanism involves transfer of alkyl to $CuCl_2$ the general scheme would be given by eq 6 (R = H, CH_3, $-CH_2-$; M = Pd(II), Pt(II), Rh(III) etc.).



Now the ratio of **1** and **2** and thus the degree of positional isomerization will depend on M. However, for each positional isomer, the stereochemistry of the products will be independent of M since they will depend on the mode of decomposition of the copper(II) alkyls, **1** and **2**. The results with cyclohexene shown in Tables I and II definitely indicate that the product distributions for the 1,2 positional isomers under one set of reaction conditions do depend on the noble metal salt used. As an example, Pd(II) consistently gives more *cis*-1,2-chloroacetate. In addition the ratio of *trans*-chloroacetate to *cis*-diacetate varies from greater than one for $PdCl_2$ to *ca.* 0.75 for $IrCl_3$ to *ca.* 0.5 for $RhCl_3$ to *ca.* 0.4 for $PtCl_2$. Similar trends are found in Table II.

The results for *cis*- and *trans*-butene also show that product distributions depend on identity of the noble metal salt. The low chloride run in Table III compares with the reaction conditions of Table IV. The following comparisons can be made.

(1) **Diacetate:Chloroacetate Ratio.** For Pd(II) (2,3 isomers) it is 0.51 for the *cis*-2-butene and 0.39 for the trans isomer. The corresponding ratios for Pt(II) are 0.15 and 0.2.

(2) **Erythro:Threo Ratio.** For Pd(II) the cis ratio is 0.43 and the trans is 2.2. The corresponding ratios for Pt(II) are 0.033 and 0.20.

(3) **Meso Diacetate:*dl* Diacetate Ratio.** For Pd(II) the cis ratio is 3.6 while the trans is 0.52. The corresponding ratios for Pt(II) are 0.11 and 1.35.

All these ratios are considerably different for Pd(II) and Pt(II).

One question that was not considered in the above discussion concerns the stereochemistry of the intermediate **2**. Depending on the stereochemistries of steps 1 and 2 this intermediate could be cis or trans with cyclohexene and threo or erythro with *cis*- or *trans*-2-butene. The two different geometric isomers might well give different modes of decomposition of **2**. The tacit assumption is that all the noble metal salts would be expected to have similar chemistry and thus the same stereochemistry for steps 1 and 2. For $PdCl_2$, step 1 has been demonstrated to have trans stereochemistry.[11]

Of course there is the possibility that, for instance, $PdCl_2$ and $PtCl_2$ may have different stereochemistries for either of the two steps. However, if that were the case, the **2** isomer from *cis*-2-butene and $PdCl_2$ would be identical with the **2** isomer from *trans*-2-butene and $PtCl_2$. However, the cis or trans isomer ratios for one metal salt do not match with the respective trans or cis isomer ratios for the other metal salt. Thus, even if the stereochemistries of steps 1 and 2 were different for $PdCl_2$ and $PtCl_2$, the arguments against the mechanism represented by this scheme would still be valid.

The product distribution for the oxidation of cyclohexene by $PdCl_2$ plus $CuCl_2$ is similar to those previously reported and consistent with a scheme involving trans acetoxypalladation followed by trans elimination of Pd(II) by acetate and cis or trans elimination of Pd(II) by chloride. The other positional isomers are formed by movement of Pd(II) around the ring in the intermediate acetoxypalladation adduct by Pd(II) hydride eliminations and readditions. In the 1,3 and 1,4 isomers the diacetates are always cis and the chloroacetates predominantly trans.

The scheme for the other noble metal salts is probably very similar. However, they give much smaller amounts of *cis*-1,2-chloroacetate than does $PdCl_2$, indicating cis elimination of noble metal by chloride is much less favored than for Pd(II).

The noble metal salts also differ considerably in their ability to move about the cyclohexane ring. Thus as can be seen from Table I, $RhCl_3$ and $OsCl_3$ gave more 3-cyclohexen-1-yl acetate than $PdCl_2$, while the other three gave none of this isomer. In this light, the much higher ratios of the 3 isomer at longer reaction times (Table II) suggests that the noble metal is catalyzing the isomerization of the 2 isomer to the 3 isomer.

The product distributions in Table III defy any simple explanation but follow some trends. Thus the amount of positional isomerization (1,3/1,2 isomer) increases with temperature and generally decreases with increasing soluble chloride concentration. As might be expected, the diacetate:chloroacetate ratio decreases with increasing soluble chloride at 25°, but, at 100°, the trends are more complicated. The ratio increases with increasing soluble chloride, for *trans*-2-butene, but increases for the cis isomer.

The meso:*dl* ratios at 25° are consistent with the scheme found for cyclohexene; trans acetoxypalladation followed by trans elimination of Pd(II). At 100°, the trends become more complicated, with the ratios differing considerably at differing soluble chloride concentrations.

Since the cyclohexene work indicated that Pd(II) can be displaced in both cis and trans fashion by chloride, the erythro:threo ratios for the 2,3-chloroacetates might be expected to be quite complicated. As can be seen from Table III, they follow no simple trends. The erythro for the *cis*-2-butene corresponds to trans addition—trans elimination (*cis*-1,2-chloroacetate in the cyclohexene system), while the threo isomer corresponds to the same series of steps for *trans*-2-butene. The fact that the trends in this case are so complicated and so different for the *cis*- and *trans*-2-butene indicates that subtle factors, such as conformational energies in the intermediate acetoxypalladation adduct, may be important. However, the present results do not permit a detailed discussion of the possible factors.

Finally one interesting aspect of the product distributions obtained from the 2-butenes is the fact that both the cis and trans isomers gave predominantly the *threo*-chloroacetate. This result could have synthetic utility, since a mixture of both isomers would give the same chloroacetate. The reason why the threo isomer is preferred for both olefins is not obvious and speculation as to possible reasons does not seem warranted.

Experimental Section

Materials. Aldrich cyclohexene was distilled and stored under N_2. The butenes were Phillips Petroleum Co. pure grade. $PdCl_2$ was purchased from Engelhardt Industries. The other noble salts were purchased from Alfa. All other chemicals were reagent grade. The preparation of dry acetic acid has been described.[17]

Experimental Procedure. The reaction procedure as well as workup of the reaction mixture has been described for both cyclohexene[11] and the butenes.[7] Product analyses were carried out by vapor phase chromatography with a 15-ft 10% UCON 75h column on Gas-Chrom Z. For the cyclohexene oxidation products, the column was programmed from 130 to 200° at 2.4°/min, while for the butenes it was programmed from 110 to 170° at 2.4°/min. The preparation of the standards the cyclohexene oxidation has been described,[11] as has the preparation of most of the standards for the butene oxidation.[7] The *meso*- and *dl*-2,3-diacetates were prepared by the acetylation of the corresponding glycols which were kindly supplied by Dr. E. J. Vandenberg of Hercules. The *threo*- and *erythro*-2,3-chloro alcohols were prepared by the reaction of *cis*- and *trans*-2,3-epoxybutane with HCl, respectively.[18] They were acetylated to give the chloroacetates.

Acknowledgments. The author gratefully acknowledges the technical assistance of Mr. F. Kriss.

Registry No.—$CuCl_2$, 7447-39-4; $PdCl_2$, 7647-10-1; $PtCl_2$, 10025-65-7; $RhCl_3$, 10049-07-7; $RuCl_3$, 10049-08-8; $IrCl_3$, 10025-83-9; $OsCl_3$, 13444-93-4; cyclohexene, 110-83-8; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; 1-butene, 106-98-9.

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(14) $RuCl_3$ was found to give saturated esters with the more easily oxidized ethylene under extreme conditions. Using the same reaction mixture as in Table I but with 1000 psig ethylene pressure in place of cyclohexene and running for 12 hr at 100°, 0.24 *M* ethylene glycol mono- and diacetate were produced.

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